Conversion of Benzoin into 9,10-Phenanthrenequinone by Photocyclisation

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Table 3. The reaction of (5) with KO_2.[a]

Solvent	Time/h	(5) (%)	(1) (%)
HMPA	24	95.0	3.8
DMF	72	80.0	19.2
DMSO	36	2.6	97.3

[a] Conditions as in Table 1.

other active oxygen species such as hydroxyl radicals and hydrogen peroxide by disproportionation,[2,3] the nature of the genuine active species in the reaction is difficult to determine. However, hydroxyl radicals can be ruled out, because imidazolones are obtained even in DMSO (see Table 2), which is known to be a hydroxyl radical scavenger.[8] A plausible mechanism for the formation of the imidazolones (**7**) and (**8**) from the thymine derivatives (**4**) and (**6**) is shown in Scheme 1. It is considered that in the double-stranded DNA there are no active hydrogens on the thymidine units, because they are included inside the double helix in a hydrogen-bonded state. Therefore we propose that this type of transformation of thymidine by superoxide might take place in biological systems under certain circumstances.

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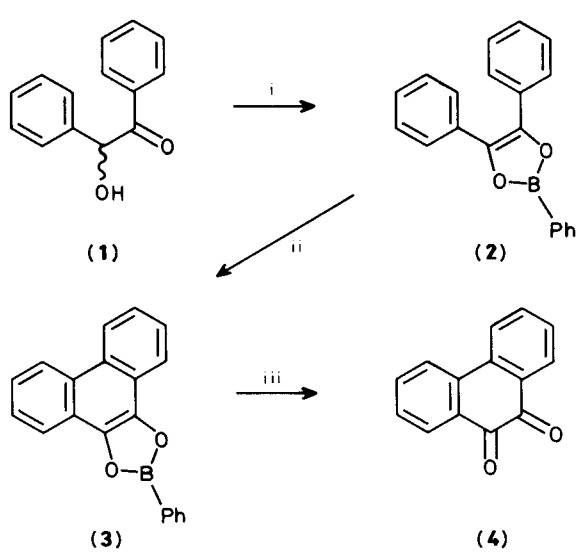
Benzoin is converted into 9,10-phenanthrenequinone by photocyclisation of its adduct with phenylboric acid, followed by hydrolysis of the photoproduct.

In connection with our efforts towards a short total synthesis of methoxatin,[1] the coenzyme of quinoproteins,[2] we needed a mild procedure to effect the conversion of a stilbene derivative into the analogous 9,10-phenanthrenequinone. Classically, this is done by oxidative photocyclisation of stilbene[3] followed by oxidation of the resulting phenanthrene to 9,10-phenanthrenequinone using CrO_3 or similar aggressive oxidants.[4] As the latter conditions were not suitable for our purpose we tried to devise a method in which a stilbene, already carrying at least one oxygen substituent on its double bond, is cyclised to the analogous phenanthrene which is now easily oxidised with Fremy's salt[5] or other mild oxidants[4] to the 9,10-phenanthrenequinone.

We have now developed a route which converts benzoin (**1**) into 9,10-phenanthrenequinone (**4**) in two simple steps (Scheme 1). Reaction of (**1**) with phenylboric acid gave the known 2,4,5-triphenyl-1,3-dioxoborole (**2**)[6] in excellent yield.† As this compound is forced into a *cis* conformation the *trans–cis* isomerisation which must precede the photocyclisation of *trans*-stilbenes is now effectively bypassed. Indeed, photocyclisation of (**2**)[7] in benzene with diphenyl diselenide as mild oxidant‡ proceeded readily to give the crystalline phenanthrene (**3**) (m.p. 200—204 °C) in 54% yield (work-up A).§



Scheme 1. *Reagents and conditions*: i, $PhB(OH)_2$; ii, *hν*, PhSeSePh; iii, $NaOH/H_2O$, air.

† *Reagents and conditions*: Benzene, azeotropic reflux, 4 h.

‡ Use of air as oxidant led to rapid decomposition.

§ *Reagents and conditions*: A solution of (**2**) (200 mg) and diphenyl diselenide (472 mg) in dry benzene (300 ml), sparged with argon 20 min before and during the reaction, was irradiated in a photochemical apparatus (Applied Photophysics) with a 450 W medium pressure mercury lamp through a pyrex sleeve (cutoff region: 290—330 nm) for 2 h 40 min. Work-up A: the solvent was evaporated and the residue crystallised from hexane. Work-up B: the solution was extracted with 1 M aq. NaOH, dried (Na_2SO_4) and evaporated, and the residue was crystallised from hexane.

Interestingly, upon hydrolysis of (3) with methanol, aqueous base, or even on t.l.c. plates the only product observed was (4) and not a trace of the analogous dihydro compound was found. The instantaneous autoxidation of 9,10-dihydroxyphenanthrene has been observed before.[8] As a consequence (4) could be isolated directly from the photolysis mixture in 84% yield after an aqueous work up which removed boric acid and simultaneously served to oxidise the presumed dihydroquinone to (4) (work-up B).§ Melting point (204—208 °C) and mixed melting point with an authentic sample (205—209 °C) confirmed its identity, as did the i.r. spectrum.

We are currently attempting to apply this methodology to the synthesis of methoxatin.

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Regioselective Ring Openings of 2,3-Epoxy Alcohols with Ammonium Halides and Sodium Benzenethiolate Supported on Zeolite CaY

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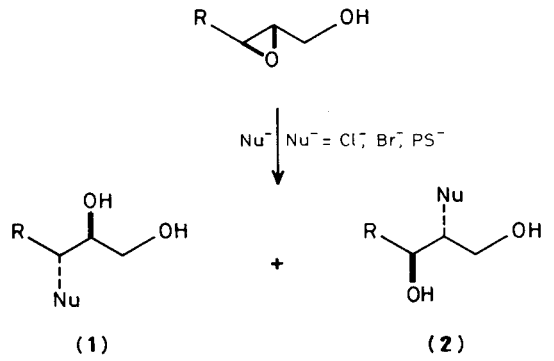
Highly regioselective ring openings of 2,3-epoxy alcohols have been performed by use of zeolite-supported ammonium halides or sodium benzenethiolate; the reactivities of these reagents are highly dependent on the conditions of their preparation.

Since optically pure 2,3-epoxy alcohols are available by Sharpless asymmetric epoxidation,[1] regioselective ring openings of epoxy alcohols with nucleophiles have been frequently utilized in the course of asymmetric syntheses of natural products.[2]

We have demonstrated that sodium azide supported on calcium ion-exchanged Y-type zeolite (CaY) reacts with 2,3-epoxy alcohols to give 3-azido 1,2-diols exclusively.[3] In order further to explore the utility of zeolite-supported reagents, we have now investigated selective ring openings of *trans*-2,3-epoxy alcohols with halide and thiolate ions; these reactions have not been accomplished with high regioselectivity hitherto.

Halide or thiolate ions (Cl^-, Br^-, or PhS^-) were attached to zeolite CaY as follows. In a round-bottomed flask (30 ml) zeolite CaY (cation contents Ca^{2+} 67%, Na^+ 33%; prepared from NaY by ion exchange[4]) (0.8 g) was immersed in a solution of NH_4Cl (3 mmol),† NH_4Br (3 mmol),† or PhSNa (2 mmol) in an impregnation solvent (3—30 ml).‡ The solvent was slowly evaporated off at 20—40 °C and 20 Torr. The amount of residual impregnation solvent contained in the supported reagent was estimated by weight increase.§



(1) (2)

A suspended mixture of the supported reagent (abbreviated NH_4X/CaY or PhSNa/CaY) and a *trans*-2,3-epoxy 1-ol (1 mmol) in an appropriate solvent (5 ml) was stirred under the conditions listed in Table 1. Methanol (6 ml) was added¶ and the mixture was stirred for 0.5 h at room temperature. Solid material was then filtered off and the filtrate was evaporated. The ring opening products were purified on silica gel as a mixture of regioisomers. The regioisomeric ratio was determined by capillary g.l.c. (PEG-HT or OV-1; 25 m) after

† As the loading of NH_4X on CaY decreases, the reactivity of the supported reagent increases. A loading of *ca.* 4 mmol of NH_4X per g of CaY is sufficient for practical use.

‡ The amount of solvent depends on the solubility of NH_4X and PhSNa.

§ The amount of residual impregnation solvent in the supported reagent can be controlled by adjusting the evaporation temperature and time.

¶ The addition of methanol is necessary for products to be desorbed from zeolite. When water is used instead of methanol, it is often difficult to extract products from an aqueous layer completely.